

# Formation of Prebiotic Molecules in Interstellar and Cometary Ices

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**Abstract.** We report here on our lab studies of ice photochemistry of large organic molecules under cometary conditions. We focus on polycyclic aromatic hydrocarbons (PAHs), their photoproducts, and their similarities to molecules seen in living systems today. We note that these kinds of compounds are seen in meteorites and we propose an explanation for both their formation and their observed deuterium enrichments.

## 1. Introduction

Comets, meteorites, and dust particles fell in profusion on the early Earth and these extraterrestrial objects are replete with complex organic molecules, which may have played a role in the origin and evolution of life. Perhaps the most abundant class of complex carbon containing compounds found in extraterrestrial objects are polycyclic aromatic hydrocarbons (PAHs) and, as we shall see, the photoproducts of PAHs are very similar to molecules that are important in living systems today.

PAHs are ubiquitous in the ISM, perhaps accounting for 20% of the cosmic carbon, (Dwek et al. 1997; Allamandola et al. 1999) and their spectral features are observed emitting from planetary nebulae, reflection nebulae, H II regions, and the diffuse interstellar medium (ISM) (Allamandola et al. 1989; Schutte et al. 1998). They have also been observed in absorption toward protostellar objects embedded in dense interstellar molecular clouds (Smith et al. 1989; Sellgren et al. 1995). These PAHs, seen in absorption in dense clouds, are presumably frozen into icy mantles on grains because at the temperatures characteristic of these clouds (10-50 K) the PAHs should condense (Sandford & Allamandola 1993). Ices in these clouds are processed by UV photons even in the densest regions (Prasad & Tieländer 1983).

We have shown that the UV photolysis of coronene in low-temperature H<sub>2</sub>O ices produces ketones, ethers, alcohols, and partially reduced aromatics known as H<sub>n</sub>-PAHs (Fig.1; Bernstein et al. 1999a). More recently we have

demonstrated that the H atoms on the PAHs can be replaced by D atoms as a result of irradiation in D<sub>2</sub>O-rich ices (Sandford et al. 1999). These results are very interesting because H atoms on PAHs are not considered to be labile, and PAHs represent a major carrier of D excesses in primitive meteorites (Kerridge et al. 1987). Thus, the photolysis of PAHs in interstellar ices may provide an explanation for the aromatics observed in meteorites and their deuterium enrichment.

## 2. Results

### 2.1. Atom Addition

Figure 2 presents the  $\mu\text{L}^2\text{MS}$  spectra of coronene ( $\text{C}_{24}\text{H}_{12}$ ), and that of the nonvolatile residues resulting from the 10 minute UV irradiation per layer of coronene in H<sub>2</sub>O and D<sub>2</sub>O ices at  $\sim 15$  K. The large peak that appears in all three spectra near 300 amu arises from unreacted coronene. The small peaks near 301 and 302 amu in the spectrum of the coronene standard (Fig. 2c), are caused by the natural abundance of the  $^{13}\text{C}$  isotopes in coronene, which also contribute to these peaks in the other two spectra. The peaks at 316, 332, and 348 amu in the spectra of the UV irradiated coronene-H<sub>2</sub>O and coronene-D<sub>2</sub>O ices correspond to the addition of one, two, and three oxygen atoms, respectively, to the coronene starting material. In Figure 2b the smaller peaks at 318 and 334 amu correspond to the addition of two H atoms to the mono- and di-oxidized coronenes at 316 and 332 amu, respectively.

### 2.2. Deuterium Exchange

In the mass spectrum of the UV-irradiated coronene-D<sub>2</sub>O mixture in Figure 2a, the peaks at 300, 316, 332, and 348 amu (coronene and coronene plus 1, 2, and 3 oxygens, respectively) are each followed by a series of peaks decreasing in intensity with increasing mass over the 301-312, 317-328, 333-344, and 349-354 amu mass ranges. These demonstrate the exchange of D atoms from the D<sub>2</sub>O ice matrix for H atoms on the coronene and its photoproducts. After only 10 minutes of photolysis a *majority* of the oxidized coronenes have exchanged at least one H atom for a D atom from the D<sub>2</sub>O ice. During this exposure period even the unoxidized coronene starting material has become appreciably deuterated (as is demonstrated by the peaks over the 301-312 amu range). This exchange of H for D, represented schematically in Figure 3a, was somewhat unexpected. Aromatic C-H bonds are normally not labile, even at much higher temperatures than those employed in our experiments (Hart 1979). This H/D exchange is not seen in control experiments when we freeze and thaw  $\text{C}_{24}\text{H}_{12}$  in D<sub>2</sub>O without photolysis. Clearly the exchange is facilitated by exposure to UV radiation and occurs very rapidly with at least one third of the unoxidized coronene acquiring one or more D atoms after only 10 minutes of UV photolysis (Fig. 2a).

### 2.3. Coronene Oxidation Enhances H/D Exchange

The different mass patterns produced by the deuterated species with and without added oxygen (Figures 2 and 3) indicate that the extent of exchange of H and

D between the coronene and the ice matrix is greater for oxidized coronene than for unoxidized coronene. This enhanced exchange is not surprising since oxidized PAHs have an additional way to exchange H atoms that reside on the same aromatic rings as the oxygen that is unavailable to unoxidized PAHs. This involves keto-enol tautomerism, the process that inter-converts the alcohol and ketone forms (Hart 1979; Figure 3b). The two H atoms associated with the oxidized ring are labile, allowing H atoms on oxidized coronenes to exchange with D atoms from the ice far more rapidly than unoxidized coronene.

### 3. Astrophysical Implications

#### 3.1. Interstellar Deuterium Levels and UV Fluxes

The extent to which interstellar PAHs deuterated in interstellar ices will depend on the concentration of deuterium in the ices and the UV fluences to which they are exposed. Recent measurements of the ratio of HDO to H<sub>2</sub>O in interstellar ice grain mantles in three dense molecular clouds yielded D/H ratios ranging from  $8 \times 10^{-4}$  to  $1 \times 10^{-2}$  (Teixeira et al. 1999). This is consistent with models of fractionation during gas-grain reactions occurring on the surfaces of the ices (Tielens 1992), thus, both observation and theory suggest that D/H ratios of  $10^{-3}$ - $10^{-2}$  are likely to be common in interstellar ice mantles.

We have demonstrated that  $H \leftrightarrow D$  exchange is rapid under experimental conditions analogous to those in the interstellar medium, with even brief exposures to UV radiation cause PAHs in ices to exchange measurable amounts of hydrogen. Thus, these processes could account for aromatics being deuterium-enriched to the level seen in the Murchison meteorite ( $D/H \sim 15 \times 10^{-4}$ ; Kerridge et al. 1987).

#### 3.2. Relevance to Meteoritic Materials

If the photolysis of PAHs in ices is responsible for a significant fraction of the deuterium enrichments of the aromatics in meteorites, we predict that meteoritic aromatics will show characteristic patterns of deuteration that are consistent with our observations and differ from those predicted by other D-enrichment processes for PAHs. For example, whereas unimolecular photo-dissociation provides largest enrichments for PAHs in the 10-40 C size range and diminish with increasing carbon number (Allamandola et. al. 1989), photolysis of PAHs in ices probably would not. Instead, the degree of deuterium enrichment should correspond to reactivity, and hence molecular structure. If a size effect exists, it will probably favor larger PAHs, inasmuch as larger PAHs tend to ionize more easily or better stabilize ion intermediates.

Furthermore, D enrichment of PAHs by photolysis in ice should put deuteria in locations that correlate with the reactions that have occurred. Specifically, replacement of the H on an aromatic C-H with a D from the ice (§2.1 and Figure 3a) results in a partially deuterated PAH, but the structure remains unchanged. Such plain aromatic C-H or C-D bonds will survive subsequent non-radiative processes such as dissolution in liquid water, as opposed to D atoms that are on an alcohol or are adjacent to either an aromatic alcohol or a ketone (§2.2 and Figure 3b) that are acquired more rapidly but could be reset

during subsequent aqueous alteration, such as is believed to have occurred on the parent bodies of many meteorites, including the CM carbonaceous chondrite Murchison (Zolensky & McSween 1988 for a review). Finally, the rate of D-atom addition to coronene (§2.1 and Figure 3c) is slower than the exchange processes but results in deuterated (cyclic) aliphatic domains, groups (-CH<sub>2</sub>-, -CD<sub>2</sub>-) with concomitant loss of aromaticity in that ring. These C-H and C-D bonds are not labile and are chemically distinct from the others.

The presence of PAHs, oxidized PAHs, and H<sub>n</sub>-PAHs in carbonaceous chondrites (Cronin & Chang 1993) is qualitatively consistent with photo-processing of aromatics in ice grains. The further observation that the aromatic materials in these meteorites are enriched in deuterium (Kerridge et al. 1987) is compatible with deuteration driven by PAH photolysis in D-enriched ices. We predict that if this process is really responsible for the deuterium enrichments of a significant portion of the aromatic compounds in meteorites, then the abundance of aromatic deuterium should show some dependence on the structure of aromatics and their chemical side groups.

#### 4. Bio(Astronomical) Implications

These oxidized PAHs that are formed in our experiments are not just meteoritic curiosities, they are also common in living systems and have biochemical activity (Fig. 4). For example, Juglone, which is found in walnut and pecan shells and Lawsone, an ingredient in Henna, are just oxidized naphthalenes. Aloe, an anti-inflammatory natural product often added to skin cream, is basically an oxidized anthracene. The active ingredient in St. Johns Wort (an over the counter anti-depressant), Hypericin, is essentially an oxidized Dibenzo[fg,op]anthracene. Naphthaquinones (oxidized naphthalenes bearing two ketones) perform an important function in electron transport, the process by which plants convert light energy into chemical energy. Furthermore, PAHs strongly absorb UV radiation so they may have acted as UV shields on the early earth, back before there was an ozone layer. Perhaps aromatic quinones, having the capacity to both absorb radiation and act in electron transport, may have been the first molecules that our ancestors used to harness light energy or carry out some other useful function (Bernstein et al. 1999b). The essence is this, perhaps certain extraterrestrial molecules were not just a source of reduced carbon to be altered by terrestrial processes, but were directly involved in pre-biotic and biotic reactions.

#### 5. Conclusions

Coronene (and other PAHs) rapidly become oxidized when UV irradiated in water ices under conditions mimicking those in dense interstellar clouds. The molecules that result include aromatic alcohols, ketones, ethers, and H<sub>n</sub>-PAHs. These kinds of molecules are seen in meteorites, expected in comets, and thus were probably delivered to the early earth by small impactors and dust particles. Given that these kinds of molecules play crucial roles in living systems today, perhaps they were involved in the origin or evolution of life on this planet.

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## Figure Captions

Figure 1 - Molecular structures produced by the UV irradiation of coronene-H<sub>2</sub>O ice samples. Oxygen adds to form ketone and alcohol side groups and H adds to form aliphatic edge structures (H<sub>n</sub>-PAHs) (see Bernstein et al. 1999).

Figure 2 - The mass spectra of (a) the room temperature residue from a short UV irradiation of coronene (C<sub>24</sub>H<sub>12</sub>; 300 amu) in D<sub>2</sub>O at ~15 K, compared with (b) the room temperature residue from a similar irradiation of coronene in H<sub>2</sub>O at ~15 K, and (c) a coronene standard deposited into H<sub>2</sub>O at ~15 K, and warmed to room temperature but not photolyzed. The radiation causes oxidation of the coronene and some H addition. The top spectrum shows that UV photolysis drives rapid H/D exchange between the ice matrix and the aromatics.

Figure 3 - Coronene photo-reactions that lead to deuterium enrichment. (a) The exchange of fully aromatic C-H bonds requires UV radiation. (b) Hydrogen exchange via keto-enol tautomerism. Only H on carbon atoms next to a C=O and next to or on a C-OH group are subject to this exchange mechanism. This exchange can occur in the absence of UV radiation. (c) The UV stimulated addition of D atoms across a double bond to yield an aliphatic ring.

Figure 4 - A comparison between several polycyclic aromatic hydrocarbons and some natural products.

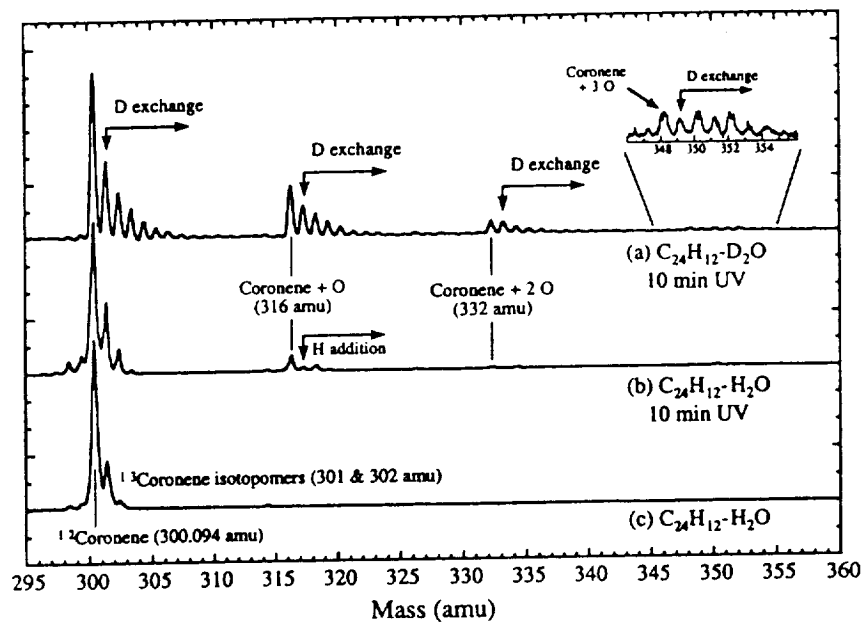


Figure 1

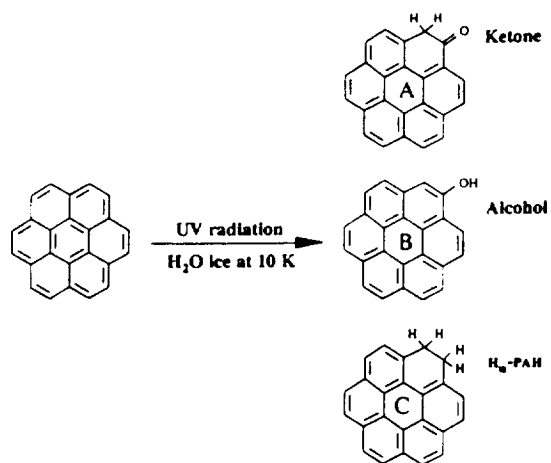




Figure 3

